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(54) **Pressure responsive electrically conductive materials**

(57) A pressure sensitive electrically conductive material comprising a non-conductive matrix of flexible elastomeric material, for example silicone or polyurethane rubber. The matrix contains electrically conductive particles, all the particles being of silicon, desirably in the size range of from 1 to 300 microns.

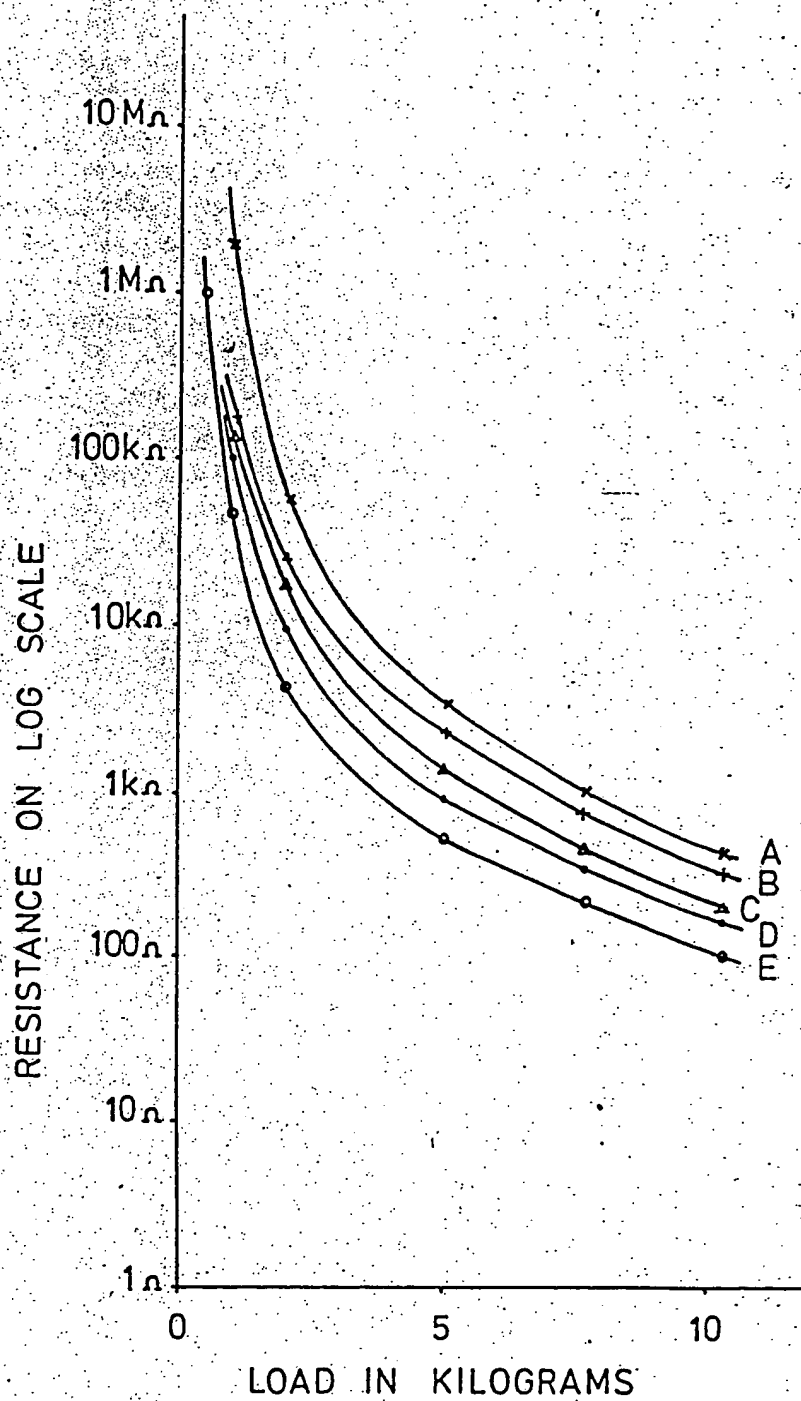


FIG. 1

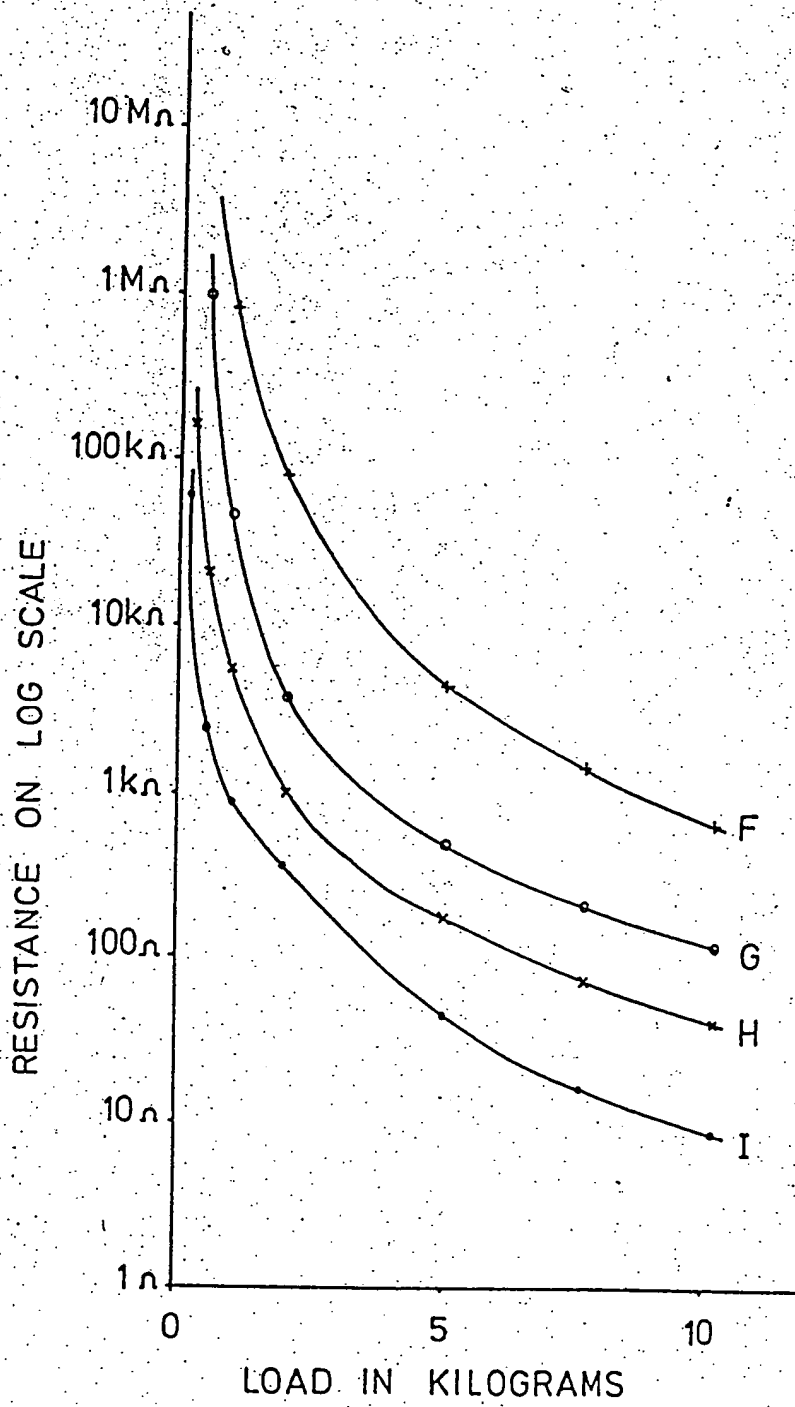


FIG. 2

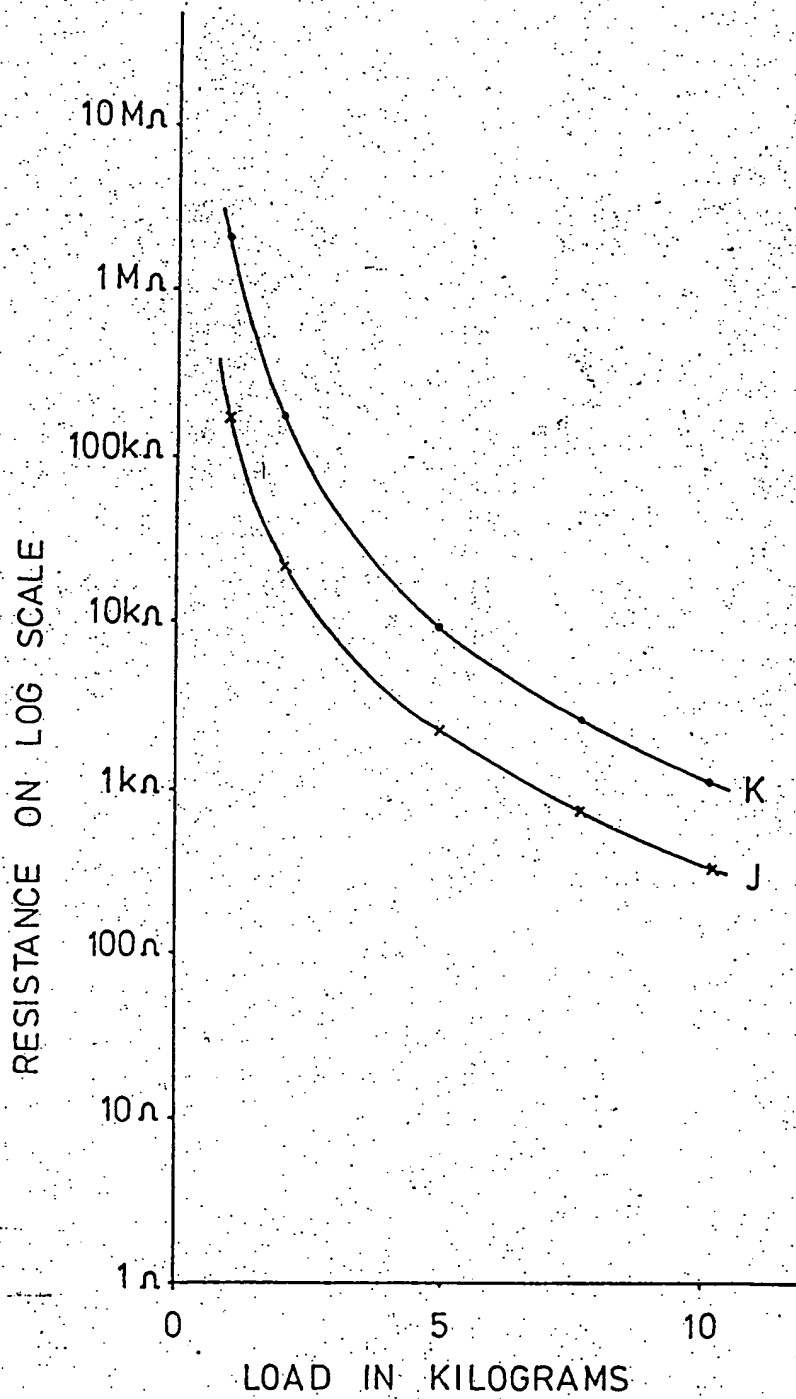


FIG. 3

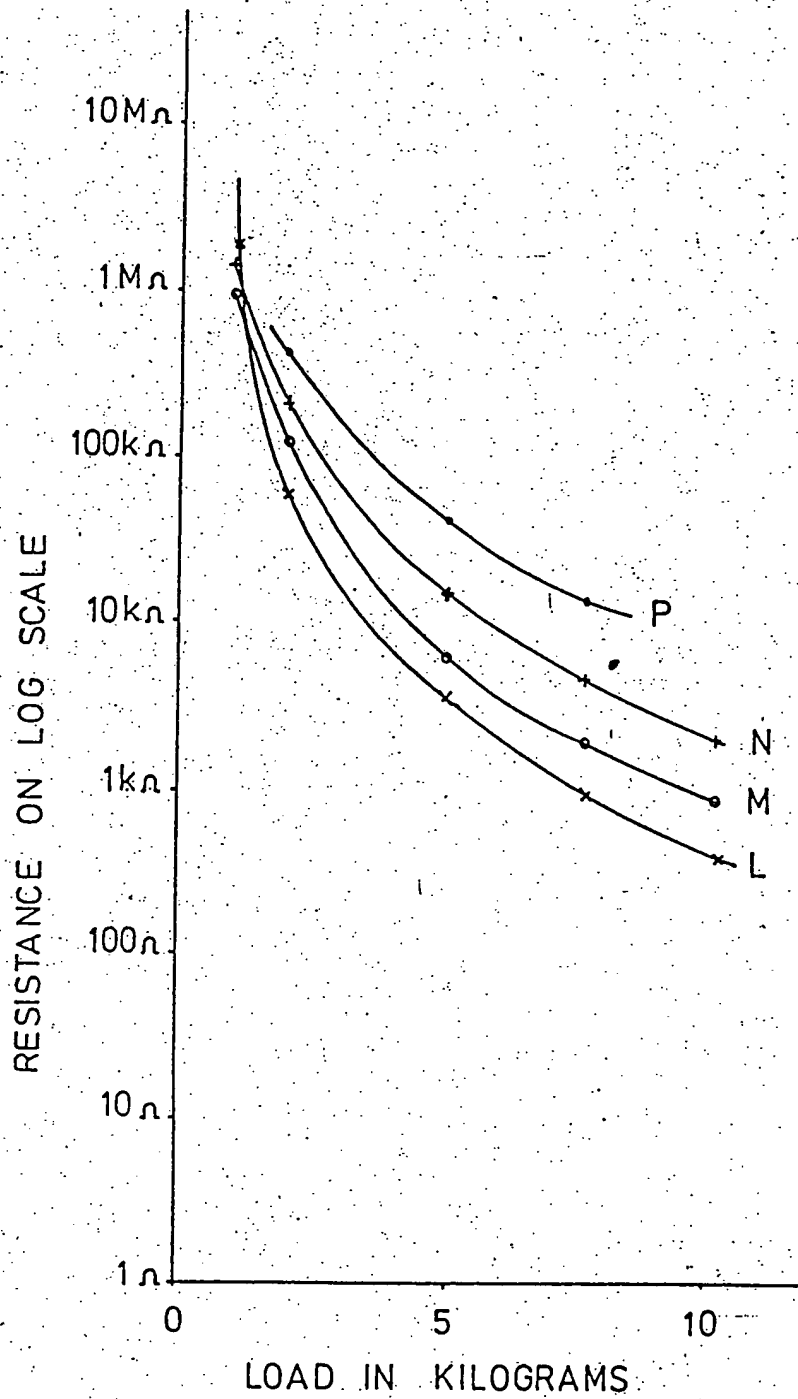


FIG. 4

SPECIFICATION

Pressure responsive electrically conductive materials

- 5 This invention relates to pressure sensitive electrically conductive materials. Many composite materials have now been proposed based on the mixing of electrically conductive particles into an electrically insulating elastomer which is subsequently shaped and cured. The resultant product is electrically non-conductive, but is rendered conductive when the material is deformed. 5
- The principal workers in the field of these materials have all recognised the difficulties in providing an
- 10 industrially acceptable material, and there are only a few manufacturers in the world who produce pressure responsive conductors on an industrial scale. Various problems that have been noted are lack of uniform electrical characteristics, inadequate mechanical strength and durability, undue variations in electrical properties of the material with repeated pressure applications and delay in electrical response. Such difficulties, and brief surveys of the developments of this type of material are described in the patent
- 15 literature in such specifications as GB-A-1561189, US-A-4302361, US-A-4138369, US-A-4028276 and US-A-3806471. 15
- Those specifications are all concerned with the selection of electrically conductive materials for incorporation into an elastomeric matrix and the method of incorporating the conductive materials in order to obtain an acceptable product. Many of the products described therein will form a material that is suitable
- 20 for use in a switching context, that is a material which exhibits a rapid and large drop in resistance when the pressure applied thereto reaches a certain level. Below that level the high resistance of the material makes it an effective insulator, while below the level the resistance drops to a figure such that the material is an effective conductor. Such materials are thus ideal for use as pressure-sensitive switches. However, none of the known prior art has put forward a practical proposal for an inexpensive pressure sensitive material that
- 25 will exhibit a resistance or conductivity curve that exhibits a gradual change over a wide range of applied pressures, thus being capable of providing an electrical output signal that is a smooth function of applied pressure. The invention seeks to provide a pressure responsive electrically conductive material that possesses this important property, and that can also be compounded to meet common industrial requirements for this type of material. 25
- 30 According to the invention a pressure sensitive electrically conductive material comprises a non-conductive matrix of flexible elastomeric material, the matrix containing electrically conductive particles, all such particles being particles of silicon. 30
- There have been prior proposals to incorporate silicon into a pressure sensitive electrically conductive material, but only in combination with other electrically conductive particles. Thus, US-A-3806471 suggests
- 35 that silicon particles can be combined with copper aluminium or iron particles, and US-A-4028276 discloses that silicon particles can be used in conjunction with particles of such conductive materials as titanium carbide and mixtures of cobalt and molybdenum. In each case the resulting materials are suitable for switch applications, exhibiting a rapid drop in resistance when a given pressure level is reached. There is no suggestion in either document that silicon can be used alone as the conductive material, and it is most
- 40 surprising to find that when it is so used the resulting filled matrix has the property that resistance is a smooth function of applied pressure over a wide pressure range. Furthermore, it has been found that silicon-loaded elastomer in accordance with the invention can very simply be prepared to exhibit required resistance/pressure characteristics, merely by simple changes of such variables as filler loading and sheet thickness. Pressure sensitive elements may thus readily be prepared that will, for example, have high
- 45 sensitivity at low pressures or low sensitivity over wide pressure ranges. 45
- The silicon used in the invention is preferably in powdered form with the particles having a size range of from 1 to 300 microns, although it may be more desirable to avoid particles having a size in excess of 200 microns. The preferred range of particle sizes is from 40 to 150 microns.
- The silicon is preferably undoped, i.e. it has not been treated to incorporate trace impurities of the
- 50 materials usually used in silicon semi-conductors. Freely available chemical grade silicon powder has been found perfectly satisfactory for use in the invention. 50
- Preferably the silicon particles make up between 30% and 60% of the volume of the material. Alternatively or additionally the particles preferably are present in from 100 to 300 parts per hundred parts by weight of matrix material (phr). Below the preferred lower limits, it may be found that unacceptably high compression
- 55 needs to be applied to the material to cause the required drop in resistance, while above the upper limit the material in its state of rest may be found to be too conductive due to contact between the conductive particles. 55
- The elastomeric matrix may be formed from any suitable polymeric material or blend thereof as long as it is electrically insulating and exhibits the required properties. Representative of suitable elastomers are
- 60 silicon rubbers, whether of the condensation reaction, addition reaction or vinyl group containing type, rubbery condensation polymers such as polyurethane rubber obtained by reaction of polyisocyanates with polyalkylene glycols, ethylene propylene-non-conjugated diene rubbers, natural rubber, synthetic polyisoprene rubber, styrene butadiene rubber, nitrile-butadiene rubber, halogenated hydrocarbon rubbers such as elastomeric chloroprene rubber, fluoroolefin rubber, chlorosulfonated polyethylene, thermoplastic
- 65 elastomers such as ethylene-vinyl acetate copolymers, and plasticizer containing thermoplastic resins. 65

Other non-conductive materials such as solvents, plasticising agents, stabilizers, pigments, colouring agents and extending oils may be incorporated into the matrix composition. Such composition may contain fillers such as silica, silicates, kaolin, mica, talc, carbonates or alumina. Generally speaking, the matrix material should be compounded so that it can resist a high-intensity electric field, has good electrically insulating properties and the mechanical properties appropriate to the end use. In some cases these properties include low permanent set and high elongation at break. In other fields it may be advantageous for the matrix to be of cellular material, and any suitable blowing agent or other expanding system may then be compounded with the elastomer. Solvent levels may be adjusted to provide a material capable of being worked in a particular way to give a finished product. For example, silicone elastomers without solvent may be moulded or spread, with moderate levels of solvent added they may be cast, and with high levels of solvent they may be screen printed or painted onto a suitable substrate.

The filler materials may be mixed with the elastomeric matrix material in any suitable manner. Mixing is facilitated if the matrix material is in liquid form, (whether using solvent or not) however, it is possible to effect mixing into a solid elastomer. The aim should be to obtain a reasonably uniform dispersion of the filler particles throughout the matrix. After mixing, a cross-linking system is added to the mixture which is then cured to any required shape. The cured material may be de-gassed if necessary. For many uses a room temperature vulcanising material is used, for ease in compounding and casting and for better control of particle distribution. When materials with better mechanical properties are required, however, high temperature vulcanising materials may be used. Alternatively, the properties of room temperature vulcanising materials may be improved by appropriate compounding ingredients.

It is particularly preferred to use a silicone or a polyurethane rubber, which can readily be compounded to give the required properties, and can be vulcanised at room temperature.

A particularly preferred material comprises powdered, undoped, chemical grade silicon loaded into a silicone rubber matrix, the silicon being present in 150 to 270 phr.

Most usually the material will be cured in the form of a thin flat sheet, which may then be cut into individual elements of required size. Preferred sheet thicknesses are from 0.15 to 3 mm, more preferably from 0.2 to 1.5 mm. It is important that any given element be of substantially uniform thickness within a close tolerance, eg. 1%. Elements moulded from identical compositions and under identical conditions but to different thicknesses are found to have widely different electrical characteristics.

The invention will now be described in more detail with reference to the following examples thereof, given in conjunction with the accompanying drawings in which Figures 1 to 4 are all graphs of resistance on a logarithmic scale against applied load.

Example 1

Batches of material were made up from Ambersil Silcoset 105 RTV (a room temperature vulcanising silicone rubber) together with undoped, chemical grade silicon powder supplied by BDH Chemicals Limited under their reference 30066. The particle size of the silicon powder was such that 1.9% by weight was retained on a 100 mesh sieve, 53.1% by weight retained on a 200 mesh sieve, 21.1% by weight retained on a 300 mesh sieve, 16.8% by weight retained on a 425 mesh sieve and the remaining 7.1% passed through the 425 mesh sieve. Mesh sizes are given according to ASTM E11. This represents a range of particle sizes that is roughly from 160 to 10 microns.

Mixing was effected by first adding curing agent 'A' as supplied with the silicon rubber to the rubber, and stirring the mixture. Subsequently 70 parts by weight of toluene per 100 parts by weight rubber were added to the mixture, and then the silicon powder was gradually added and also stirred in. The material was cast into open moulds so that the toluene solvent could evaporate during curing, and was allowed to cure at room temperature.

Samples were cut from the cured sheets and their resistance was measured at different applied loads. The results are given below.

Run	Sheet thickness (mm)	phr Silicon
A	0.76	190
B	0.76	210
C	0.76	230
D	0.76	250
E	0.76	270
F	1.35	270
G	0.76	270
H	0.41	270
I	0.23	270

The resistance-load graphs for runs A to E are shown in Figure 1 and those for runs F to I in Figure 2. In each case it will be seen that a smooth curve is obtained over a wide range of applied load values. Figure 1 illustrates that higher silicon loading leads to lower resistance for the same thickness of sheet, while Figure 2

illustrates that for the same loading of silicon thinner sheets have lower resistance than thicker sheets. The compound and sheet thickness can thus readily be tailored for specific applications.

Example 2

- 5 The silicon powder referred to in Example 1 was powder ball milled for 24 hours in order to reduce its size. Of the milled powder 0.6% by weight was retained on a 100 mesh sieve, 3.8% on a 200 mesh sieve, 14.9% on a 300 mesh sieve, 50% on a 425 mesh sieve and the remaining 30.7% passed through the 425 mesh sieve. Following the technique described in Example 1, 250 phr of the powder as received was loaded into an Ambersil Silcoset 105 RTV rubber matrix, and 250 phr of the ball milled powder was loaded into the same matrix material. The compression-loaded graphs for the respective runs J and K are shown in Figure 3, illustrating that the material with the smaller particle silicon filler had a higher resistance, and again illustrating the smoothness of the curve over a wide range of applied loads.

Example 3

- 15 The aforesaid silicon powder in the form as supplied by BDH Chemicals Limited was incorporated into a matrix of Ambersil Silcoset 105 RTV and formed into sheets 0.76 mm thick. In run L the silicon was added to the rubber in the presence of 70 phr toluene as solvent and the mixture was cast into sheets. In run M mixing took place without solvent and the material was sheet moulded to the required thickness. In runs N and P respectively 10 phr and 20 phr palm oil were added to the rubber before addition of the silicon powder and the material was spread to the required thickness. Figure 4 shows the resistance-load curves obtained from the four materials, all exhibiting the smooth curves over a wide load range that are typical of the materials of the invention.

CLAIMS

- 25 1. A pressure sensitive electrically conductive material comprising a non-conductive matrix of flexible elastomeric material, the matrix containing electrically conductive particles, all such particles being particles of silicon.
2. A material according to claim 1 in which the silicon is in powdered form, the particles having a size range of from 1 to 300 microns.
- 30 3. A material according to claim 1 in which the silicon is in powdered form, the particles having a size range of from 40 to 150 microns.
4. A material according to any one of the preceding claims in which the silicon is undoped.
5. A material according to any one of the preceding claims in which the silicon is in the form of chemical grade silicon powder.
- 35 6. A material according to any one of the preceding claims in which the silicon particles constitute from 30% to 60% by volume of the material.
7. A material according to any one of the preceding claims in which the silicon particles are present in from 100 to 300 parts per 100 parts by weight of elastomeric material.
- 40 8. A material according to any one of the preceding claims in which the silicon particles are present in from 150 to 270 parts per 100 parts by weight of elastomeric material.
9. A material according to any one of the preceding claims in which the elastomeric material is a silicone rubber.
10. A material according to any one of the preceding claims in which the elastomeric material is a polyurethane rubber.
- 45 11. A pressure sensitive electrically conductive material according to claim 1, substantially as herein described.
12. A pressure sensitive electrically conductive material substantially as described in any one of the foregoing Examples.